

## 1.0 Introduction

The objective of the report is to provide a reasoned and documented discussion on the technical issues associated with the measurement and selection of partition (or distribution) coefficient,  $K_d$ ,<sup>1,2</sup> values and their use in formulating the retardation factor,  $R_f$ . The contaminant retardation factor ( $R_f$ ) is the parameter commonly used in transport models to describe the chemical interaction between the contaminant and geological materials (*i.e.*, soil, sediments, rocks, and geological formations, henceforth simply referred to as soils<sup>3</sup>). It includes processes such as surface adsorption, absorption into the soil structure, precipitation, and physical filtration of colloids. Specifically, it describes the rate of contaminant transport relative to that of groundwater. This report is provided for technical staff from EPA and other organizations who are responsible for prioritizing site remediation and waste management decisions. The two-volume report describes the conceptualization, measurement, and use of the  $K_d$  parameter; and geochemical aqueous solution and sorbent properties that are most important in controlling the adsorption/retardation behavior of a selected set of contaminants.

This review is not meant to assess or judge the adequacy of the  $K_d$  approach used in modeling tools for estimating adsorption and transport of contaminants and radionuclides. Other approaches, such as surface complexation models, certainly provide more robust mechanistic approaches for predicting contaminant adsorption. However, as one reviewer of this volume noted, “ $K_d$ ’s are the coin of the realm in this business.” For better or worse, the  $K_d$  model is integral part of current methodologies for modeling contaminant and radionuclide transport and risk analysis.

The  $K_d$  concept, its use in fate and transport computer codes, and the methods for the measurement of  $K_d$  values are discussed in detail in Volume I and briefly introduced in Chapters 2 and 3 in Volume II. Particular attention is directed at providing an understanding of: (1) the use of  $K_d$  values in formulating  $R_f$ , (2) the difference between the original thermodynamic  $K_d$  parameter derived from the ion-exchange literature and its “empiricized” use in contaminant

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<sup>1</sup> Throughout this report, the term “partition coefficient” will be used to refer to the  $K_d$  “linear isotherm” sorption model. It should be noted, however, that the terms “partition coefficient” and “distribution coefficient” are used interchangeably in the literature for the  $K_d$  model.

<sup>2</sup> A list of acronyms, abbreviations, symbols, and notation is given in Appendix A. A list of definitions is given in Appendix B

<sup>3</sup> The terms “sediment” and “soil” have particular meanings depending on one’s technical discipline. For example, the term “sediment” is often reserved for transported and deposited particles derived from soil, rocks, or biological material. “Soil” is sometimes limited to referring to the top layer of the earth’s surface, suitable for plant life. In this report, the term “soil” was selected with concurrence of the EPA Project Officer as a general term to refer to all unconsolidated geologic materials.

transport codes, and (3) the explicit and implicit assumptions underlying the use of the  $K_d$  parameter in contaminant transport codes.

The  $K_d$  parameter is very important in estimating the potential for the adsorption of dissolved contaminants in contact with soil. As typically used in fate and contaminant transport calculations, the  $K_d$  is defined as the ratio of the contaminant concentration associated with the solid to the contaminant concentration in the surrounding aqueous solution when the system is at equilibrium. Soil chemists and geochemists knowledgeable of sorption processes in natural environments have long known that generic or default  $K_d$  values can result in significant errors when used to predict the impacts of contaminant migration or site-remediation options. To address some of this concern, modelers often incorporate a degree of conservatism into their calculations by selecting limiting or bounding conservative  $K_d$  values. For example, the most conservative (*i.e.*, maximum) estimate from the perspective of off-site risks due to contaminant migration through the subsurface natural soil and groundwater systems is to assume that the soil has little or no ability to slow (retard) contaminant movement (*i.e.*, a minimum bounding  $K_d$  value). Consequently, the contaminant would travel in the direction and at the rate of water. Such an assumption may in fact be appropriate for certain contaminants such as tritium, but may be too conservative for other contaminants, such as thorium or plutonium, which react strongly with soils and may migrate  $10^2$  to  $10^6$  times more slowly than the water. On the other hand, when estimating the risks and costs associated with on-site remediation options, a maximum bounding  $K_d$  value provides an estimate of the maximum concentration of a contaminant or radionuclide sorbed to the soil. Due to groundwater flow paths, site characteristics, or environmental uncertainties, the final results of risk and transport calculations for some contaminants may be insensitive to the  $K_d$  value even when selected within the range of technically-defensible, limiting minimum and maximum  $K_d$  values. For those situations that are sensitive to the selected  $K_d$  value, site-specific  $K_d$  values are essential.

The  $K_d$  is usually a measured parameter that is obtained from laboratory experiments. The 5 general methods used to measure  $K_d$  values are reviewed. These methods include the batch laboratory method, the column laboratory method, field-batch method, field modeling method, and  $K_{oc}$  method. The summary identifies what the ancillary information is needed regarding the adsorbent (soil), solution (contaminated ground-water or process waste water), contaminant (concentration, valence state, speciation distribution), and laboratory details (spike addition methodology, phase separation techniques, contact times). The advantages, disadvantages, and, perhaps more importantly, the underlying assumptions of each method are also presented.

A conceptual overview of geochemical modeling calculations and computer codes as they pertain to evaluating  $K_d$  values and modeling of adsorption processes is discussed in detail in Volume I and briefly described in Chapter 4 of Volume II. The use of geochemical codes in evaluating aqueous speciation, solubility, and adsorption processes associated with contaminant fate studies is reviewed. This approach is compared to the traditional calculations that rely on the constant  $K_d$  construct. The use of geochemical modeling to address quality assurance and technical defensibility issues concerning available  $K_d$  data and the measurement of  $K_d$  values is also

discussed. The geochemical modeling review includes a brief description of the EPA's MINTEQA2 geochemical code and a summary of the types of conceptual models it contains to quantify adsorption reactions. The status of radionuclide thermodynamic and contaminant adsorption model databases for the MINTEQA2 code is also reviewed.

The main focus of Volume II is to: (1) provide a "thumb-nail sketch" of the key geochemical processes affecting the sorption of a selected set of contaminants; (2) provide references to related key experimental and review articles for further reading; (3) identify the important aqueous- and solid-phase parameters controlling the sorption of these contaminants in the subsurface environment; and (4) identify, when possible, minimum and maximum conservative  $K_d$  values for each contaminant as a function key geochemical processes affecting their sorption. The contaminants chosen for the first phase of this project include cadmium, cesium, chromium, lead, plutonium, radon, strontium, thorium, tritium ( $^3\text{H}$ ), and uranium. The selection of these contaminants by EPA and PNNL project staff was based on 2 criteria. First, the contaminant had to be of high priority to the site remediation or risk assessment activities of EPA, DOE, and/or NRC. Second, because the available funding precluded a review of all contaminants that met the first criteria, a subset was selected to represent categories of contaminants based on their chemical behavior. The six nonexclusive categories are:

- Cations - cadmium, cesium, plutonium, strontium, thorium, and uranium(VI).
- Anions - chromium(VI) (as chromate) and uranium(VI).
- Radionuclides - cesium, plutonium, radon, strontium, thorium, tritium ( $^3\text{H}$ ), and uranium.
- Conservatively transported contaminants - tritium ( $^3\text{H}$ ) and radon.
- Nonconservatively transported contaminants - other than tritium ( $^3\text{H}$ ) and radon.
- Redox sensitive elements - chromium, plutonium, and uranium.

The general geochemical behaviors discussed in this report can be used by analogy to estimate the geochemical interactions of similar elements for which data are not available. For example, contaminants present primarily in anionic form, such as Cr(VI), tend to adsorb to a limited extent to soils. Thus, one might generalize that other anions, such as nitrate, chloride, and U(VI)-anionic complexes, would also adsorb to a limited extent. Literature on the adsorption of these 3 solutes show no or very little adsorption.

The concentration of contaminants in groundwater is controlled primarily by the amount of contaminant present at the source; rate of release from the source; hydrologic factors such as dispersion, advection, and dilution; and a number of geochemical processes including aqueous geochemical processes, adsorption/desorption, precipitation, and diffusion. To accurately predict contaminant transport through the subsurface, it is essential that the important geochemical processes affecting contaminant transport be identified and, perhaps more importantly, accurately described in a mathematically and scientifically defensible manner. Dissolution/precipitation and adsorption/desorption are usually the most important processes affecting contaminant interaction with soils. Dissolution/precipitation is more likely to be the key process where chemical nonequilibrium exists, such as at a point source, an area where high contaminant concentrations

exist, or where steep pH or oxidation-reduction (redox) gradients exist. Adsorption/desorption will likely be the key process controlling contaminant migration in areas where chemical steady state exist, such as in areas far from the point source. Diffusion flux spreads solute via a concentration gradient (*i.e.*, Fick's law). Diffusion is a dominant transport mechanism when advection is insignificant, and is usually a negligible transport mechanism when water is being advected in response to various forces.

## 2.0 The $K_d$ Model

The simplest and most common method of estimating contaminant retardation is based on the partition (or distribution) coefficient,  $K_d$ . The  $K_d$  parameter is a factor related to the partitioning of a contaminant between the solid and aqueous phases. It is an empirical unit of measurement that attempts to account for various chemical and physical retardation mechanisms that are influenced by a myriad of variables. The  $K_d$  metric is the most common measure used in transport codes to describe the extent to which contaminants are sorbed to soils. It is the simplest, yet least robust model available. A primary advantage of the  $K_d$  model is that it is easily inserted into hydrologic transport codes to quantify reduction in the rate of transport of the contaminant relative to groundwater, either by advection or diffusion. Technical issues, complexities, and shortcomings of the  $K_d$  approach to describing contaminant sorption to soils are summarized in detail in Chapter 2 of Volume I. Particular attention is directed at issues relevant to the selection of  $K_d$  values from the literature for use in transport codes.

The partition coefficient,  $K_d$ , is defined as the ratio of the quantity of the adsorbate adsorbed per mass of solid to the amount of the adsorbate remaining in solution at equilibrium. For the reaction



the mass action expression for  $K_d$  is

$$K_d = \frac{\text{Mass of Adsorbate Sorbed}}{\text{Mass of Adsorbate in Solution}} = \frac{A_i}{C_i} \quad (2.2)$$

where  $A$  = free or unoccupied surface adsorption sites

$C_i$  = total dissolved adsorbate remaining in solution at equilibrium

$A_i$  = amount of adsorbate on the solid at equilibrium.

The  $K_d$  is typically given in units of ml/g. Describing the  $K_d$  in terms of this simple reaction assumes that  $A$  is in great excess with respect to  $C_i$  and that the activity of  $A_i$  is equal to 1.

Chemical retardation,  $R_f$ , is defined as,

$$R_f = \frac{v_p}{v_c}, \quad (2.3)$$

where  $v_p$  = velocity of the water through a control volume

$v_c$  = velocity of contaminant through a control volume.

The chemical retardation term does not equal unity when the solute interacts with the soil; almost always the retardation term is greater than 1 due to solute sorption to soils. In rare cases, the

retardation factor is actually less than 1, and such circumstances are thought to be caused by anion exclusion (See Volume I, Section 2.8). Knowledge of the  $K_d$  and of media bulk density and porosity for porous flow, or of media fracture surface area, fracture opening width, and matrix diffusion attributes for fracture flow, allows calculation of the retardation factor. For porous flow with saturated moisture conditions, the  $R_f$  is defined as

$$R_f = 1 + \frac{\rho_b}{n_e} K_d \quad (2.4)$$

where  $\rho_b$  = porous media bulk density (mass/length<sup>3</sup>)  
 $n_e$  = effective porosity of the media at saturation.

The  $K_d$  parameter is valid only for a particular adsorbent and applies only to those aqueous chemical conditions (*e.g.*, adsorbate concentration, solution/electrolyte matrix) in which it was measured. Site-specific  $K_d$  values should be used for site-specific contaminant and risk assessment calculations. Ideally, site-specific  $K_d$  values should be measured for the range of aqueous and geological conditions in the system to be modeled. However, literature-derived  $K_d$  values are commonly used for screening calculations. Suitable selection and use of literature-derived  $K_d$  values for use in screening calculations of contaminant transport is not a trivial matter. Among the assumptions implicit with the  $K_d$  construct is: (1) only trace amounts of contaminants exist in the aqueous and solid phases, (2) the relationship between the amount of contaminant in the solid and liquid phases is linear, (3) equilibrium conditions exist, (4) equally rapid adsorption and desorption kinetics exists, (5) it describes contaminant partitioning between 1 sorbate (contaminant) and 1 sorbent (soil), and (6) all adsorption sites are accessible and have equal strength. The last point is especially limiting for groundwater contaminant models because it requires that  $K_d$  values should be used only to predict transport in systems chemically identical to those used in the laboratory measurement of the  $K_d$ . Variation in either the soil or aqueous chemistry of a system can result in extremely large differences in  $K_d$  values.

A more robust approach than using a single  $K_d$  to describe the partitioning of contaminants between the aqueous and solid phases is the parametric- $K_d$  model. This model varies the  $K_d$  value according to the chemistry and mineralogy of the system at the node being modeled. The parametric- $K_d$  value, unlike the constant- $K_d$  value, is not limited to a single set of environmental conditions. Instead, it describes the sorption of a contaminant in the range of environmental conditions used to create the parametric- $K_d$  equations. These types of statistical relationships are devoid of causality and therefore provide no information on the mechanism by which the radionuclide partitioned to the solid phase, whether it be by adsorption, absorption, or precipitation. Understanding these mechanisms is extremely important relative to estimating the mobility of a contaminant.

When the parametric- $K_d$  model is used in the transport equation, the code must also keep track of the current value of the independent variables at each point in space and time to continually update the concentration of the independent variables affecting the  $K_d$  value. Thus, the code must

track many more parameters and some numerical solving techniques (such as closed-form analytical solutions) can no longer be used to perform the integration necessary to solve for the  $K_d$  value and/or retardation factor,  $R_F$ . Generally, computer codes that can accommodate the parametric- $K_d$  model use a chemical subroutine to update the  $K_d$  value used to determine the  $R_F$ , when called by the main transport code. The added complexity in solving the transport equation with the parametric- $K_d$  sorption model and its empirical nature may be the reasons this approach has been used sparingly.

Mechanistic models explicitly accommodate for the dependency of  $K_d$  values on contaminant concentration, charge, competing ion concentration, variable surface charge on the soil, and solution species distribution. Incorporating mechanistic adsorption concepts into transport models is desirable because the models become more robust and, perhaps more importantly from the standpoint of regulators and the public, scientifically defensible. However, truly mechanistic adsorption models are rarely, if ever, applied to complex natural soils. The primary reason for this is because natural mineral surfaces are very irregular and difficult to characterize. These surfaces consist of many different microcrystalline structures that exhibit quite different chemical properties when exposed to solutions. Thus, examination of the surface by virtually any experimental method yields only averaged characteristics of the surface and the interface.

Less attention will be directed to mechanistic models because they are not extensively incorporated into the majority of EPA, DOE, and NRC modeling methodologies. The complexity of installing these mechanistic adsorption models into existing transport codes is formidable. Additionally, these models also require a more extensive database collection effort than will likely be available to the majority of EPA, DOE, and NRC contaminant transport modelers. A brief description of the state of the science is presented in Volume I primarily to provide a paradigm for sorption processes.

### 3.0 Methods, Issues, and Criteria for Measuring $K_d$ Values

There are 5 general methods used to measure  $K_d$  values: the batch laboratory method, laboratory flow-through (or column) method, field-batch method, field modeling method, and  $K_{oc}$  method. These methods and the associated technical issues are described in detail in Chapter 3 of Volume I. Each method has advantages and disadvantages, and perhaps more importantly, each method has its own set of assumptions for calculating  $K_d$  values from experimental data. Consequently, it is not only common, but expected that  $K_d$  values measured by different methods will produce different values.

#### 3.1 *Laboratory Batch Method*

Batch tests are commonly used to measure  $K_d$  values. The test is conducted by spiking a solution with the element of interest, mixing the spiked solution with a solid for a specified period of time, separating the solution from the solid, and measuring the concentration of the spiked element remaining in solution. The concentration of contaminant associated with the solid is determined by the difference between initial and final contaminant concentration. The primary advantage of the method is that such experiments can be completed quickly for a wide variety of elements and chemical environments. The primary disadvantage of the batch technique for measuring  $K_d$  is that it does not necessarily reproduce the chemical reaction conditions that take place in the real environment. For instance, in a soil column, water passes through at a finite rate and both reaction time and degree of mixing between water and soil can be much less than those occurring in a laboratory batch test. Consequently,  $K_d$  values from batch experiments can be high relative to the extent of sorption occurring in a real system, and thus result in an estimate of contaminant retardation that is too large. Another disadvantage of batch experiments is that they do not accurately simulate desorption of the radionuclides or contaminants from a contaminated soil or solid waste source. The  $K_d$  values are frequently used with the assumption that adsorption and desorption reactions are reversible. This assumption is contrary to most experimental observations that show that the desorption process is appreciably slower than the adsorption process, a phenomenon referred to as hysteresis. The rate of desorption may even go to zero, yet a significant mass of the contaminant remains sorbed on the soil. Thus, use of  $K_d$  values determined from batch adsorption tests in contaminant transport models is generally considered to provide estimates of contaminant remobilization (release) from soil that are too large (*i.e.*, estimates of contaminant retention that are too low).

#### 3.2 *Laboratory Flow-Through Method*

Flow-through column experiments are intended to provide a more realistic simulation of dynamic field conditions and to quantify the movement of contaminants relative to groundwater flow. It is the second most common method of determining  $K_d$  values. The basic experiment is completed by passing a liquid spiked with the contaminant of interest through a soil column. The column experiment combines the chemical effects of sorption and the hydrologic effects of groundwater flow through a porous medium to provide an estimate of retarded movement of the contaminant



of interest. The retardation factor (a ratio of the velocity of the contaminant to that of water) is measured directly from the experimental data. A  $K_d$  value can be calculated from the retardation factor. It is frequently useful to compare the back-calculated  $K_d$  value from these experiments with those derived directly from the batch experiments to evaluate the influence of limited interaction between solid and solution imposed by the flow-through system.

One potential advantage of the flow-through column studies is that the retardation factor can be inserted directly into the transport code. However, if the study site contains different hydrological conditions (*e.g.*, porosity and bulk density) than the column experiment, then a  $K_d$  value needs to be calculated from the retardation factor. Another advantage is that the column experiment provides a much closer approximation of the physical conditions and chemical processes occurring in the field site than a batch sorption experiment. Column experiments permit the investigation of the influence of limited spatial and temporal (nonequilibrium) contact between solute and solid have on contaminant retardation. Additionally, the influence of mobile colloid facilitated transport and partial saturation can be investigated. A third advantage is that both adsorption or desorption reactions can be studied. The predominance of 1 mechanism of adsorption or desorption over another cannot be predicted *a priori* and therefore generalizing the results from 1 set of laboratory experimental conditions to field conditions is never without some uncertainty. Ideally, flow-through column experiments would be used exclusively for determining  $K_d$  values, but equipment cost, time constraints, experimental complexity, and data reduction uncertainties discourage more extensive use.

### 3.3 Other Methods

Less commonly used methods include the  $K_{oc}$  method, *in-situ* batch method, and the field modeling method. The  $K_{oc}$  method is a very effective indirect method of calculating  $K_d$  values, however, it is only applicable to organic compounds. The *in-situ* batch method requires that paired soil and groundwater samples be collected directly from the aquifer system being modeled and then measuring directly the amount of contaminant on the solid and liquid phases. The advantage of this approach is that the precise solution chemistry and solid phase mineralogy existing in the study site is used to measure the  $K_d$  value. However, this method is not used often because of the analytical problems associated with measuring the exchangeable fraction of contaminant on the solid phase. Finally, the field modeling method of calculating  $K_d$  values uses groundwater monitoring data and source term data to calculate a  $K_d$  value. One key drawback to this technique is that it is very model dependent. Because the calculated  $K_d$  value are model dependent and highly site specific, the  $K_d$  values must be used for contaminant transport calculations at other sites.

### 3.4 Issues

A number of issues exist concerning the measurement of  $K_d$  values and the selection of  $K_d$  values from the literature. These issues include: using simple versus complex systems to measure  $K_d$  values, field variability, the “gravel issue,” and the “colloid issue.” Soils are a complex mixture

containing solid, gaseous, and liquid phases. Each phase contains several different constituents. The use of simplified systems containing single mineral phases and aqueous phases with 1 or 2 dissolved species has provided valuable paradigms for understanding sorption processes in more complex, natural systems. However, the  $K_d$  values generated from these simple systems are generally of little value for importing directly into transport models. Values for transport models should be generated from geologic materials from or similar to the study site. The “gravel issue” is the problem that transport modelers face when converting laboratory-derived  $K_d$  values based on experiments conducted with the <2-mm fraction into values that can be used in systems containing particles >2 mm in size. No standard methods exist to address this issue. There are many subsurface soils dominated by cobbles, gravel, or boulders. To base the  $K_d$  values on the <2-mm fraction, which may constitute only <1 percent of the soil volume but is the most chemically reactive fraction, would grossly overestimate the actual  $K_d$  of the aquifer. Two general approaches have been proposed to address this issue. The first is to assume that all particles >2-mm has a  $K_d = 0$  ml/g. Although this assumption is incorrect (*i.e.*, cobbles, gravel, and boulders do in fact sorb contaminants), the extent to which sorption occurs on these larger particles may be small. The second approach is to normalize laboratory-derived  $K_d$  values by soil surface area. Theoretically, this latter approach is more satisfying because it permits some sorption to occur on the >2-mm fraction and the extent of the sorption is proportional to the surface area. The underlying assumptions in this approach are that the mineralogy is similar in the less than 2- and greater than 2-mm fractions and that the sorption processes occurring in the smaller fraction are similar to those that occur in the larger fraction.

Spatial variability provides additional complexity to understanding and modeling contaminant retention to subsurface soils. The extent to which contaminants partition to soils changes as field mineralogy and chemistry change. Thus, a single  $K_d$  value is almost never sufficient for an entire study site and should change as chemically important environmental conditions change. Three approaches used to vary  $K_d$  values in transport codes are the  $K_d$  look-up table approach, the parametric- $K_d$  approach, and the mechanistic  $K_d$  approach. The extent to which these approaches are presently used and the ease of incorporating them into a flow model varies greatly. Parametric- $K_d$  values typically have limited environmental ranges of application. Mechanistic  $K_d$  values are limited to uniform solid and aqueous systems with little application to heterogeneous soils existing in nature. The easiest and the most common variable- $K_d$  model interfaced with transport codes is the look-up table. In  $K_d$  look-up tables, separate  $K_d$  values are assigned to a matrix of discrete categories defined by chemically important ancillary parameters. No single set of ancillary parameters, such as pH and soil texture, is universally appropriate for defining categories in  $K_d$  look-up tables. Instead, the ancillary parameters must vary in accordance to the geochemistry of the contaminant. It is essential to understand fully the criteria and process used for selecting the values incorporated in such a table. Differences in the criteria and process used to select  $K_d$  values can result in appreciable different  $K_d$  values. Examples are presented in this volume.

Contaminant transport models generally treat the subsurface environment as a 2-phase system in which contaminants are distributed between a mobile aqueous phase and an immobile solid phase

(*e.g.*, soil). An increasing body of evidence indicates that under some subsurface conditions, components of the solid phase may exist as colloids<sup>1</sup> that may be transported with the flowing water. Subsurface mobile colloids originate from (1) the dispersion of surface or subsurface soils, (2) decementation of secondary mineral phases, and (3) homogeneous precipitation of groundwater constituents. Association of contaminants with this additional mobile phase may enhance not only the amount of contaminant that is transported, but also the rate of contaminant transport. Most current approaches to predicting contaminant transport ignore this mechanism not because it is obscure or because the mathematical algorithms have not been developed, but because little information is available on the occurrence, the mineralogical properties, the physicochemical properties, or the conditions conducive to the generation of mobile colloids. There are 2 primary problems associated with studying colloid-facilitated transport of contaminants under natural conditions. First, it is difficult to collect colloids from the subsurface in a manner which minimizes or eliminates sampling artifacts. Secondly, it is difficult to unambiguously delineate between the contaminants in the mobile-aqueous and mobile-solid phases.

Often  $K_d$  values used in transport models are selected to provide a conservative estimate of contaminant migration or health effects. However, the same  $K_d$  value would not provide a conservative estimate for clean-up calculations. Conservatism for remediation calculations would tend to err on the side of underestimating the extent of contaminant desorption that would occur in the aquifer once pump-and-treat or soil flushing treatments commenced. Such an estimate would provide an upper limit to time, money, and work required to extract a contaminant from a soil. This would be accomplished by selecting a  $K_d$  from the upper range of literature values.

It is incumbent upon the transport modeler to understand the strengths and weaknesses of the different  $K_d$  methods, and perhaps more importantly, the underlying assumption of the methods in order to properly select  $K_d$  values from the literature. The  $K_d$  values reported in the literature for any given contaminant may vary by as much as 6 orders of magnitude. An understanding of the important geochemical processes and knowledge of the important ancillary parameters affecting the sorption chemistry of the contaminant of interest is necessary for selecting appropriate  $K_d$  value(s) for contaminant transport modeling.

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<sup>1</sup> A colloid is any fine-grained material, sometimes limited to the particle-size range of  $<0.00024$  mm (*i.e.*, smaller than clay size), that can be easily suspended (Bates and Jackson, 1980). In its original sense, the definition of a colloid included any fine-grained material that does not occur in crystalline form. The geochemistry of colloid systems is discussed in detail in sources such as Yariv and Cross (1979) and the references therein.

## 4.0 Application of Chemical Reaction Models

Computerized chemical reaction models based on thermodynamic principles may be used to calculate processes such as aqueous complexation, oxidation/reduction, adsorption/desorption, and mineral precipitation/dissolution for contaminants in soil-water systems. The capabilities of a chemical reaction model depend on the models incorporated into its computer code and the availability of thermodynamic and/or adsorption data for aqueous and mineral constituents of interest. Chemical reaction models, their utility to understanding the solution chemistry of contaminants, and the MINTEQA2 model in particular are described in detail in Chapter 5 of Volume I.

The MINTEQA2 computer code is an equilibrium chemical reaction model. It was developed with EPA funding by originally combining the mathematical structure of the MINEQL code with the thermodynamic database and geochemical attributes of the WATEQ3 code. The MINTEQA2 code includes submodels to calculate aqueous speciation/complexation, oxidation-reduction, gas-phase equilibria, solubility and saturation state (*i.e.*, saturation index), precipitation/dissolution of solid phases, and adsorption. The most current version of MINTEQA2 available from EPA is compiled to execute on a personal computer (PC) using the MS-DOS computer operating system. The MINTEQA2 software package includes PRODEFA2, a computer code used to create and modify input files for MINTEQA2.

The MINTEQA2 code contains an extensive thermodynamic database for modeling the speciation and solubility of contaminants and geologically significant constituents in low-temperature, soil-water systems. Of the contaminants selected for consideration in this project [chromium, cadmium, cesium, tritium ( $^3\text{H}$ ), lead, plutonium, radon, strontium, thorium, and uranium], the MINTEQA2 thermodynamic database contains speciation and solubility reactions for chromium, including the valence states Cr(II), Cr(III), and Cr(VI); cadmium; lead; strontium; and uranium, including the valence states U(III), U(IV), U(V), and U(VI). Some of the thermodynamic data in the EPA version have been superseded in other users' databases by more recently published data.

The MINTEQA2 code includes 7 adsorption model options. The non-electrostatic adsorption models include the activity  $K_d^{\text{act}}$ , activity Langmuir, activity Freundlich, and ion exchange models. The electrostatic adsorption models include the diffuse layer, constant capacitance, and triple layer models. The MINTEQA2 code does not include an integrated database of adsorption constants and reactions for any of the 7 models. These data must be supplied by the user as part of the input file information.

Chemical reaction models, such as the MINTEQA2 code, cannot be used *a priori* to predict a partition coefficient,  $K_d$ , value. The MINTEQA2 code may be used to calculate the chemical changes that result in the aqueous phase from adsorption using the more data intensive, electrostatic adsorption models. The results of such calculations in turn can be used to back calculate a  $K_d$  value. The user however must make assumptions concerning the composition and mass of the dominant sorptive substrate, and supply the adsorption parameters for surface-

complexation constants for the contaminants of interest and the assumed sorptive phase. The EPA (EPA 1992, 1996) has used the MINTEQA2 model and this approach to estimate  $K_d$  values for several metals under a variety of geochemical conditions and metal concentrations to support several waste disposal issues. The EPA in its “Soil Screening Guidance” determined MINTEQA2-estimated  $K_d$  values for barium, beryllium, cadmium, Cr(III), Hg(II), nickel, silver, and zinc as a function of pH assuming adsorption on a fixed mass of iron oxide (EPA, 1996; RTI, 1994). The calculations assumed equilibrium conditions, and did not consider redox potential or metal competition for the adsorption sites. In addition to these constraints, EPA (1996) noted that this approach was limited by the potential sorbent surfaces that could be considered and availability of thermodynamic data. Their calculations were limited to metal adsorption on iron oxide, although sorption of these metals to other minerals, such as clays and carbonates, is well known.

Typically, the data required to derive the values of adsorption parameters that are needed as input for adsorption submodels in chemical reaction codes are more extensive than information reported in a typical laboratory batch  $K_d$  study. If the appropriate data are reported, it is likely that a user could hand calculate a composition-based  $K_d$  value from the data reported in the adsorption study without the need of a chemical reaction model.

Chemical reaction models can be used, however, to support evaluations of  $K_d$  values and related contaminant migration and risk assessment modeling predictions. Chemical reaction codes can be used to calculate aqueous complexation to determine the ionic state and composition of the dominant species for a dissolved contaminant present in a soil-water system. This information may in turn be used to substantiate the conceptual model being used for calculating the adsorption of a particular contaminant. Chemical reaction models can be used to predict bounding, technically defensible maximum concentration limits for contaminants as a function of key composition parameters (*e.g.*, pH) for any specific soil-water system. These values may provide more realistic bounding values for the maximum concentration attainable in a soil-water system when doing risk assessment calculations. Chemical reaction models can also be used to analyze initial and final geochemical conditions associated with laboratory  $K_d$  measurements to determine if the measurement had been affected by processes such as mineral precipitation which might have compromised the derived  $K_d$  values. Although chemical reaction models cannot be used to predict  $K_d$  values, they can provide aqueous speciation and solubility information that is exceedingly valuable in the evaluation of  $K_d$  values selected from the literature and/or measured in the laboratory.